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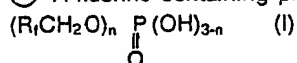
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(54) Fluorine-containing phosphate ester, its preparation and rust preventive comprising the same.

(57) A fluorine-containing phosphate ester of the formula:



wherein R<sub>1</sub> is a group containing a perfluoroalkyl polyether group and n is an integer of 1 to 3,  
is used as a rust preventive which can be homogeneously mixed with a fluorine-containing grease.

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# FLUORINE-CONTAINING PHOSPHATE ESTER, ITS PREPARATION AND RUST PREVENTIVE COMPRISING THE SAME

## BACKGROUND OF THE INVENTION

### Field of the Invention

The present invention relates to a novel fluorine-containing phosphate ester, its preparation and a rust preventive comprising the same.

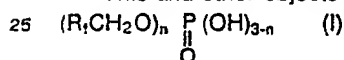
### Description of the Related Art

Since a fluorine-containing grease has properties of insulation and non-flammability, it can be used in various applications. Inorganic powder such as sodium nitrate or magnesium oxide is used as a rust preventive or a stabilizer for the fluorine-containing grease. However, the inorganic powder is not easily available in the form of fine powder and is hardly homogeneously mixed with the fluorine-containing grease. When the inorganic powder is used for a bearing, it makes big noise.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a fluorine-containing phosphate ester which is easily available, can be homogeneously mixed with the fluorine-containing grease and can be used as a rust preventive which does not make a noise.

This and other objects are achieved by a fluorine-containing phosphate ester of the formula:

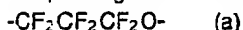


wherein  $R_1$  is a group containing a perfluoroalkyl polyether group and  $n$  is an integer of 1 to 3.

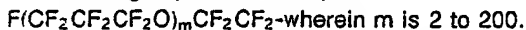
Also, the present invention provides a rust preventive comprising said fluorine-containing phosphate ester (I).

## DETAILED DESCRIPTION OF THE INVENTION

In the fluorine-containing phosphate ester (I), the perfluoroalkyl polyether group in the  $R_1$  group contains a repeating unit of the formula:

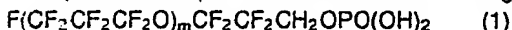


The  $R_1$  group is, for example,

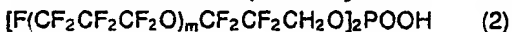


In the formula (I),  $n$  is preferably 1 or 2.

Specific examples of the fluorine-containing phosphate ester (I) are

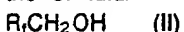


wherein  $m$  is 2 to 200, preferably 25 on the average, and



wherein  $m$  is 2 to 200, preferably 25 on the average.

The fluorine-containing phosphate ester (I) can be prepared by reacting a fluorine-containing alcohol of the formula:



wherein  $R_1$  is the same as described above, with a phosphoryl compound and then with water.

The phosphoryl compound is, for example, phosphoryl trichloride or phosphoric acid. A mixture of phosphoryl trichloride and phosphoric acid is preferably used. The mixture of phosphoryl trichloride and phosphoric acid preferably contains phosphoryl trichloride and phosphoric acid in a molar ratio of 1:2 to 1:6. The fluorine-containing alcohol may be reacted with the phosphoryl compound at a temperature of 60 to 120 °C for 2 to 6 hours.

Hydrolysis is carried out through the reaction with water. Water may be used in an amount of not less

than 10 moles per mole of the phosphoryl compound. The hydrolysis may be carried out at a temperature of 80 to 100 °C for 1 to 5 hours.

The rust preventive comprising the fluorine-containing phosphate ester (I) in which n is two is particularly preferable. The rust preventive according to the present invention can be advantageously used as the rust preventive which is added to the fluorine-containing grease, although it may be used as the thermally resistant rust preventive in applications other than the addition to the fluorine-containing grease. The rust preventive according to the present invention is easily available and can be homogeneously mixed with the fluorine-containing grease. Even if it is used for a bearing, it makes little noise.

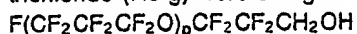
The fluorine-containing phosphate ester (I) has good mold release and can be used also as a releasing agent. It is suitably used as an extreme-pressure additive.

#### PREFERRED EMBODIMENTS OF THE INVENTION

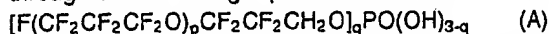
The present invention is illustrated by following Examples.

##### Example 1

In a 500 ml four-neck flask, an 85% aqueous solution of phosphoric acid (1.3 g) and phosphoryl trichloride (7.0 g) were charged and the fluorine-containing alcohol:



wherein p is 25 on the average (500 g) was dropwise added while stirring. After the reaction was carried out at 90 °C for three hours, a resultant hydrogen chloride gas was removed for three hours under a reduced pressure. Then, water (100 g) having the temperature of 90 to 95 °C was added and the hydrolysis was carried out at 95 °C for one hour while stirring. After the reaction mixture was cooled to a room temperature, it was extracted from trichlorotrifluoroethane (Daiflon S-3 manufactured by Daikin Industries Ltd.) (1 kg). Washing with water was repeated until adjusting pH of a trichlorotrifluoroethane phase to not smaller than about 4. Then, trichlorotrifluoroethane was evaporated under a reduced pressure. A residue was filtrated through a filter having a pore diameter of 0.2 μm to obtain the fluorine-containing phosphate ester:



wherein p is 25 on the average and q is 1, 2 and 3 in the molar ratio of 10/70/20. Yield: 450 g (90%).

##### Example 2

To a perfluoropolyether oil (Demnum S-65 manufactured by Daikin Industries Ltd.) (10 g), the fluorine-containing phosphate ester (0.3 g) prepared in Example 1 was added and then trichlorotrifluoroethane (10 g) was added to prepare a homogeneous solution. An iron test piece was dipped in the solution, and then removed from the solution and dried in the air. A rust prevention test was carried out by using a 100 ml polyethylene wide-mouthed container which contained a 1% aqueous solution of salt (30 ml). The test piece was placed in the container such that a portion of the test piece was in the aqueous solution and the other portion of the test piece was out of the aqueous solution. Then the container was capped and left at a room temperature for 24 hours. The test piece had no rust.

##### Comparative Example 1

A solution was prepared and the rust prevention test was carried out in the same manner as in Example 2 but the fluorine-containing phosphate ester was not used. The test piece had much rust.

##### Example 3

A fluorine-containing grease (Demnum Grease L-65 manufactured by Daikin Industries Ltd.) (20 g) was homogeneously mixed with the fluorine-containing phosphate ester prepared in Example 1 (0.6 g) to prepare a mixture grease. Then corrosion test was carried out. According to ASTM 1743-73, the mixture grease was coated on a conical roller bearing and the bearing was dipped in a 0.1% aqueous salt solution

of salt for 60 seconds. Then, the bearing was left at a room temperature under a relative humidity of 100% for 48 hours. The bearing had no corrosion.

#### 5 Comparative Example 2

The corrosion test was carried out in the same manner as in Example 3 but the fluorine-containing phosphate ester was not used. Some corroded portions were observed.

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#### Example 4

A fluorine-containing grease (Demnum Grease L-65 manufactured by Daikin Industries Ltd.) (10 g), the fluorine-containing phosphate ester prepared in Example 1 (0.3 g) and trichlorotrifluoroethane (10 g) were  
15 homogeneously mixed. Then the test was carried out in the same manner as in Example 2. The test piece had no rust.

#### Example 5

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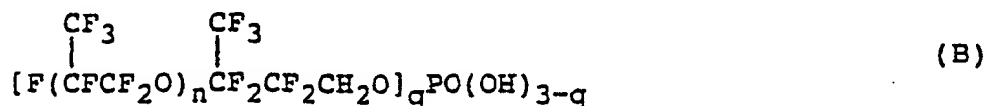
The fluorine-containing phosphate ester prepared in Example 1 (66 g) and a low-molecular weight polytetrafluoroethylene (Daikin-Polyflon TFE low polymers L-5 manufactured by Daikin Industries Ltd.) were mixed in a grinding machine to prepare a grease having the consistency of 285. The test was carried out in the same manner as in Example 3. No corrosion was observed.

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#### Comparative Example 3

The fluorine-containing compound:

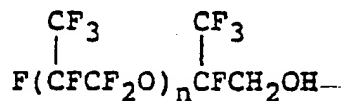
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wherein n is 16 on the average and q is 1, 2 and 3 in the molar ratio of 10/70/20, was prepared in the same manner as in Example 1 but using, as the fluorine-containing alcohol, the compound:

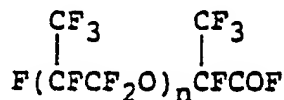
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wherein n is 16 on the average prepared from the compound:

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wherein n is 16 on the average.

Evaporation losses of the fluorine-containing phosphate ester (A) and the fluorine-containing phosphate  
55 ester (B) were measured at 250 °C. The phosphate ester (20 g) was charged in a glass cylindrical container (inner diameter: 85 mm, height: 17 mm) and the container was placed in a circulating hot air oven heated at 250 °C. After 3 hours, a loss of weight was measured.

	Dynamic viscosity at 40 ° C (cst)	Evaporation loss at 250 ° C (% by weight)
Ester (A)	162	2.3
Ester (B)	167	14.1

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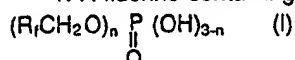
The evaporation loss is advantageously small so as to use the ester as a thermally resistant rust preventive. From the above results, it is understood that the fluorine-containing phosphate ester (A) according to the present invention has smaller evaporation loss and better than the fluorine-containing phosphate ester (B) although both have almost the same viscosity.

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### Claims

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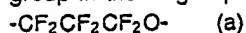
1. A fluorine-containing phosphate ester of the formula:



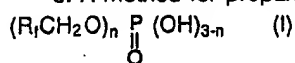
wherein  $R_f$  is a group containing a perfluoroalkyl polyether group and  $n$  is an integer of 1 to 3.

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2. The fluorine-containing phosphate ester according to claim 1, wherein the perfluoroalkyl polyether group in the  $R_f$  group contains a repeating unit of the formula:

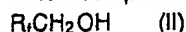


3. A method for preparing a fluorine-containing phosphate ester of the formula:



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which comprises reacting a fluorine-containing alcohol of the formula:



with a phosphoryl compound and then with water,

wherein  $R_f$  is a group containing a perfluoroalkyl polyether group and  $n$  is an integer of 1 to 3.

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4. A rust preventive comprising the fluorine-containing phosphate ester according to claim 1.

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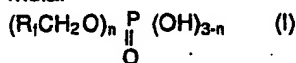
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	DE-A-2 515 374 (ASAHI DENKA K.K.K.) * Page 5, line 12 - page 6, line 6; claims 1,2 *	1	C 08 G 65/32 C 23 F 11/00
A	EP-A-0 015 592 (AGFA-GEVAERT) * Claims *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 08 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27-03-1990	Examiner WEIS R.E.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			